Technical Note

Improved Analysis of a Gas Oil Using a High-Performance Thin-Layer Chromatographic System

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Hydrocarbon-type analysis (HTA) is very useful in petrochemical analysis for determining fuel quality, evaluating the variables involved in conversion processes, elucidating reaction pathways and kinetics, and obtaining insights into the processability of a petrochemical feed or the quality of the final products.

In the case of middle distillates (e.g., gas oil), HTA is usually carried out using high-performance liquid chromatography (HPLC) with retention index (RI) detection. However, this technique presents several disadvantages that have been reported elsewhere (1) such as indirect determination of saturates and technical problems derived from RI detection.

Although thin-layer chromatography (TLC) with scanning densitometry is at present a mature analytical technique and gives some advantages over HPLC for analyzing complex samples, it has been infra-utilized in the analysis of these products mostly because of the lack of ultraviolet (UV) and fluorescent response of saturated hydrocarbons. However, saturated hydrocarbons give a fluorescent emission signal when they are spotted onto a silica gel TLC plate that has been previously impregnated with berberine sulfate and the system irradiated using a 365-nm wavelength for UV light excitation. In a recent study (2), the nature of the fluorescent emission involved in the hydrocarbon response was elucidated. Likewise, this phenomenon has been applied to petrochemical analysis in another study (1). In that study, hydrocarbon types (including saturated hydrocarbons) were successfully separated and determined in middle (e.g., gas oil) and heavy petroleum distillates using TLC–UV and fluorescence scanning densitometry with adequate precision and sensitivity.

After sample application using an autospotter, the separation of a gas oil into saturates and aromatics was performed on silica gel plates impregnated with berberine sulfate after elution with *n*-hexane (9 min) and dichloromethane (4 min), respectively. Elution was carried out in a conventional development tank. For detection, two alternative procedures were possible using the same berberine-impregnated silica gel TLC plate: (*a*) saturates were detected by berberine-induced fluorescence with excitation at 365 nm and aromatics (and polars, if any) were detected by UV (250 nm) and (*b*) saturates and aromatics were detected in the same measurement by berberine-induced fluorescence.

In the case of saturates, the magnitude of fluorescent response depends on the hydrocarbon structure (chain length), and the sensitivity of the detection can be tailored to a certain extent through control of the impregnating conditions. In the case of aromatics, the fluorescent response is mostly because of the alkylic chains of alkyl-aromatics that are present in the petroleum aromatics. However, an intrinsic fluorescent response of some aromatic moieties cannot be discarded. Therefore, the particular characteristics of alkylic chains and aromatic compounds existing in a given product will greatly influence the limit of detection for aromatics using this method.

Thus, the fluorescent response of gas oil aromatics is usually low, and several tens of micrograms of gas oil must usually be applied to give analytically useful signals when using the proposed method. This is a problem because when using large amounts, the peak response may no longer be in the linear zone of area-mass response in the berberine system for the given amount of berberine used in the impregnation. In order to solve this problem, if the amount of berberine for impregnating the plates is increased, the level of the fluorescence background of berberine will also be increased and hence the mass work range will be diminished. Likewise, on occasions, a sample overload may prevent a correct separation of spots or may give a saturation of the detector, which hinders the simultaneous determina-

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tion of both peaks. An improvement in the sensitivity of the aromatic detection should be obtained by diminishing the width of the aromatic peak.

In this work, the combined use of a band-sprayer sample applicator (Linomat IV, Camag, Muttenz, Switzerland), high-performance silica gel TLC plates (10- × 10-cm glass, 3–10-µm particle size, 60-A pore size, 0.2-mm thick layer) (Merck, Darmstadt, Germany), and a horizontal development chamber (Camag) has led to a notable improvement in the analysis of gas oil using the same conditions of excitation as in our previous study (365-nm wavelength for UV light excitation).

The main advantage of this applicator is that it can deposit a sample uniformly (at constant density) as bands by spraying
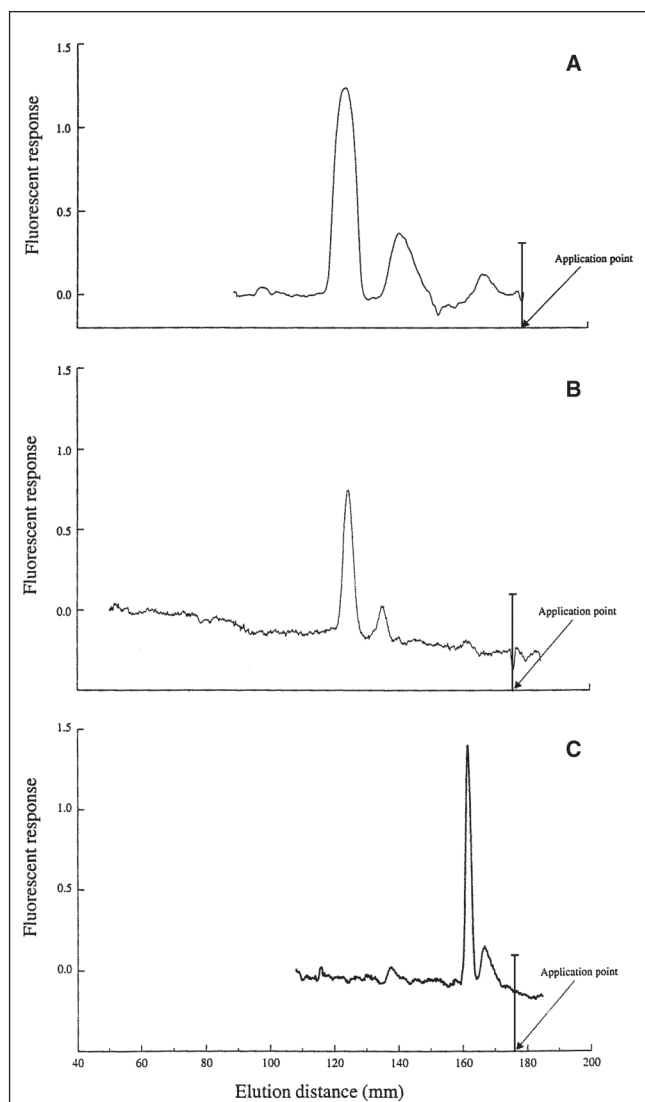
it using N_2 as the impulsion gas. Thus, the solvent is evaporated while the application is being carried out. Therefore, narrow and homogeneous bands were obtained making further separation more efficient and detection easier in regards to the autospotter, which applies samples as a spot with solvent. In this case, solvent diffusion contributes to broadening the spotted sample. Figure 1 shows the influence of the sample application technology on the peak width using TLC plates and conventional development in a vertical tank. Sample loads using Linomat IV ranged from 2 to 12 µg compared with 5–40 µg using the autospotter.

In general, when berberine-impregnated high-performance TLC plates and a horizontal development chamber are used, narrow and well-separated peaks are obtained in a short time (6 min), and only one eluant (*n*-hexane) is required for separating the peaks (Figure 1). Therefore, detection sensitivity was increased. The sample loads used were in the range of 2 to 8 µg.

Figure 2 shows the application of this improved method to two gas oils with different distributions of saturated chains. According to data from simulated distillation, GTOT has a paraffinic distribution centered in a longer chain than GOL. As a consequence of this, the berberine-induced fluorescent response of GTOT saturates is higher than that of GOL.

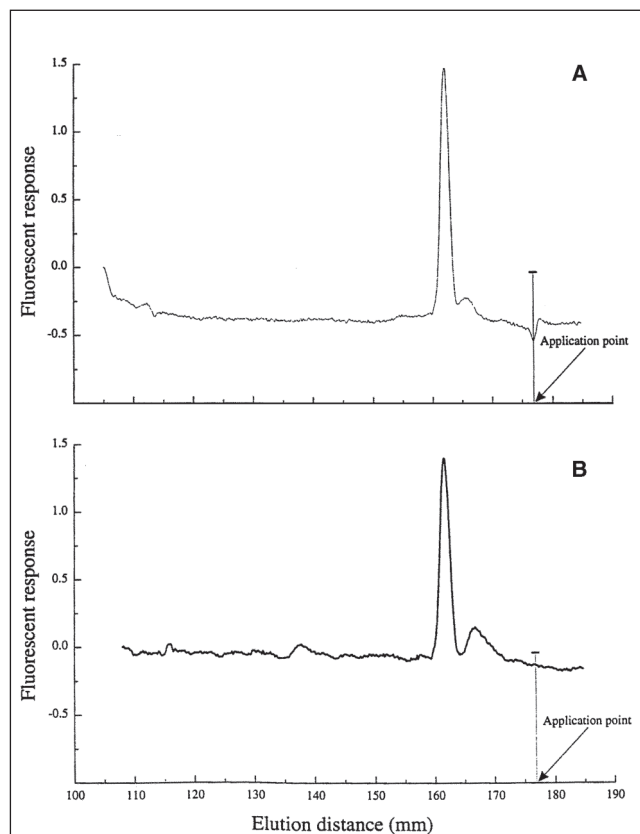The described method provides an improved way of separating

Figure 1. Analysis of a gas oil using fluorescence scanning densitometry and TLC and high-performance TLC systems on berberine-impregnated silica gel plates. 100-µg sample load, autospotter applicator, conventional development with *n*-hexane (9 min) and then dichloromethane (4 min), A; 4-µg sample load, band-sprayer applicator, conventional development with *n*-hexane (9 min) and then dichloromethane (4 min), B; 4-µg sample load, band-sprayer applicator, horizontal development with *n*-hexane (6 min), C. Conditions of impregnation in all cases: 12 mg in 200 mL of methanol during 20 s.

Figure 2. Application of the high-performance TLC system with fluorescence scanning densitometry for the analysis of two different gas oils—GOL (A) and GTOT (B). Conditions: berberine-impregnated high-performance TLC plate (12 mg in 200 mL of methanol during 20 s), band-sprayer applicator, 4-µg sample load, horizontal development with *n*-hexane (6 min).

and detecting gas oil for hydrocarbon-type determinations. The quantitative aspect of this method remains the same as previously described (1). The method proposed here can also be applied to the analysis of other petroleum-derived products.

Acknowledgments

References

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2. F.P. Cossío, A. Arrieta, V.L. Cebolla, L. Membrado, M.P. Domingo, P. Henrion, and J. Vela. Enhancement of fluorescence in thin-layer chromatography induced by the interaction between *n*-alkanes and an organic cation. *Anal. Chem.* **72:** 1759–66 (2000).